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Orientation dependence in superelastic Cu-Al-Mn-Ni micropillars

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Abstract

The superelastic behavior of single crystal Cu-Al-Mn-Ni shape memory alloy micro-pillars was studied under compression as a function of crystallographic orientation. Cylindrical pillars of about 2 μm diameter were micro-machined from targeted crystal orientations. While pillars oriented close to the [001] direction showed the largest total transformation strain (~7%), plastic deformation dominated the compressive response in the pillars milled close to the [111] direction due to their high elastic anisotropy combined with the large stresses required to induce the transformation. Shape strain contour plots were constructed for γ' and β' martensites, and the martensite start stress was calculated using the Clausius-Clapeyron equation. The same general trends are observed in both the experimental and calculated results, with some exceptions: larger transformation stresses and lower transformation strains are observed in the microsized pillars.

Keywords: Cu-Al-Ni-Mn shape memory alloys; superelastic anisotropy; Micropillars; Micro-compression test; Martensitic phase transformation.

1. Introduction

The shape memory effect relies on a martensitic phase transformation: a first order, diffusionless, solid-solid phase transformation from a high temperature phase of high symmetry to a phase with lower symmetry which is stable at lower temperatures. This transformation can be thermally or mechanically activated, and depending on which phase is stable at the testing temperature, a shape memory alloy (SMA) can exhibit either superelasticity or the shape memory effect.

Cu-based shape memory alloys have been studied extensively for the past few decades due to their excellent thermomechanical response together with their lower materials cost when compared to other shape memory alloys (e.g. NiTi, AuCd, Pt-alloys, etc). β-stabilizer elements, such as Ni and Mn, have been added to Cu-Al alloys to increase their ductility by decreasing the degree of order in the β-phase; as a result, improved shape memory properties have been reported in ternary and quaternary Cu-based alloys [1,2]. In particular, the mechanical behavior of bulk Cu-Al-Ni and Cu-Zn-Al alloys has been widely studied, in compression as well as in tension. Favorably oriented single crystals of Cu-Al-Ni shape memory alloys exhibit recoverable strains up to 10% in tension [3]. However, bulk polycrystalline Cu-based SMAs are brittle and prone to intergranular fracture during martensitic transformation due in part to their large elastic anisotropy [4,5]. For example, the stress required to induce martensitic transformation along the

[111] direction was found to be twice that required along the [001] direction in CuAlNi alloys, and the total strains in those two orientations are respectively 4 and 10% approximately [6]. Such orientation dependence is also sensitive to the mode of loading, i.e., tension vs. compression along the same axis resulting in different transformation strains [7-9].

Nano and micro-scale Cu-based SMAs have attracted attention for the past few years due to their potential to be used as actuators at the micro and nano scale in micro electro-mechanical systems (MEMS) [10-20]. Excellent superelastic behavior has been found in Cu-Al-Ni micro and nano pillars [15-18] which are able to withstand cycling over at least hundreds of cycles [16,18]. However, the study of shape memory alloys at the micro- and nano-scale is not straightforward, and some of the measured behaviors are different from those observed in nominally similar bulk materials. For example, in Ni-based SMAs, lower transformation strains and larger martensitic transformation stresses are commonly observed when the sample length scale decreases. Such size effects have been studied in NiTi [10,14,19] and Ni-Fe(Mn)-Ga micro pillars [13,21,22]. In Cu-based SMAs, San Juan and coworkers [20] have observed three different size effects: with decreasing sample size they noted (i) an increase of the critical stress for martensitic transformation, (ii) a decrease of the stress for recovery during the austenite reversion, and (iii) an apparent change of the selection rule for the martensitic variants.

The above two critical issues, namely sample size effects, and crystal orientation effects, have rarely been studied together, and to our knowledge, the combination has so far only been approached in NiTi SMAs [10,12,19]. We are not aware of any systematic investigation on orientation dependence of transformation stresses and strains in Cu-based micropillars. It is, therefore, the aim of this work to provide a first study on this issue.

2. Theoretical calculations

Cu-Al-(Ni)-(Mn) alloys transform from their cubic β phase (DO_3 or $L2_1$ type ordered structure) to either an orthorhombic γ' phase (2H stacking structure) or a β'monoclinic phase (M18R, M9R or $6M_1$ stacking structure) when cooled below the martensite finish temperature, M_f, or when an external stress is applied [1,2,23,24]. While M18R and M9R are the stacking structures most widely used in the literature to describe the β → β' transformation, several works suggest that the $6M_1$ unit cell is the one that actually forms and more accurately reflects the symmetry of the product phase [24-26], and this was therefore the monoclinic phase considered in the present work.

Transformation strain contour plots were constructed for the $6M_1$ and 2H martensites (Figure 1 a and b), respectively), based on the energy minimization theory described in [27]. Considering the lattice correspondences between the cubic DO_3 and the monoclinic $6M_1$ transformation, there are a total of 12 martensite variants of the form:

$$U_0 = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \rho & \sigma \\ 0 & \sigma & \tau \end{pmatrix} \quad (1)$$

where

$$\beta = b/a_0, \quad (2)$$

$$\rho = \frac{\alpha^2+\gamma^2+2\alpha\gamma(\sin(\theta)+\cos(\theta))}{2\sqrt{\alpha^2+\gamma^2+2\alpha\gamma\sin(\theta)}} \quad (3)$$

$$\tau = \frac{\alpha^2+\gamma^2+2\alpha\gamma(\sin(\theta)-\cos(\theta))}{2\sqrt{\alpha^2+\gamma^2+2\alpha\gamma\sin(\theta)}} \quad (4)$$

and $\sigma = \frac{\alpha^2-\gamma^2}{2\sqrt{\alpha^2+\gamma^2+2\alpha\gamma\sin(\theta)}}$ (5)

with $\alpha = \sqrt{2}a/a_0$, (6)

$$\gamma = \sqrt{2}c/a_0 \quad (7)$$

and cell parameters listed in table 1.

For the cubic to orthorhombic 2H transformation there are 6 independent lattice correspondence variants. The deformation matrix U_0 represented in the cubic basis is:

$$U_0 = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \frac{\alpha+\gamma}{2} & \frac{\alpha-\gamma}{2} \\ 0 & \frac{\alpha-\gamma}{2} & \frac{\alpha+\gamma}{2} \end{pmatrix} \quad (8)$$

Where α, β and γ are the transformation stretches defined as above and the cell parameters for the 2H martensite are defined in Table 1

Using the Bain transformation matrix (U_0) and applying the corresponding rotations (R) to obtain the other martensite variants, the transformation strain, ε_{tr}, in a direction, $\hat{e}$, is calculated as:

$$\varepsilon_{tr} = \sqrt{\hat{e}.(U^t U \hat{e})} - 1 \quad (10)$$

The value of ε_{tr} in a certain orientation is the maximum recoverable strain in compression corresponding to the formation of the most favorable martensite variant [5,26]. As can be observed in the contour strain maps of Fig. 1 a and b, in both cases under compressive stresses, larger ε_{tr} are always observed close to the (001) pole and the lowest ones are closest to the (111) pole, independently of which martensite phase forms. The difference between the two is generally subtle, being most pronounced near the (101) pole.

Based on the above theoretical transformation strains, the theoretical uniaxial stress to trigger the martensitic transformation, σ_{Ms}, is calculated using the Clausius-Clapeyron equation, $\frac{d\sigma}{dT} = \frac{-\Delta S}{V\varepsilon_{tr}}$, where the entropy change of the transformation ΔS into 2H and $6M_1$ martensites is taken as 1.54 and 1.11 J/mol °C respectively [30] and the composition-weighted average molar volume of the elements in the alloy is, V = 7.79 cm^3/mol. The test temperature and the marteniste start temperature, M_s, used in the calculations are 18°C and -36°C, respectively. The calculated σ_{Ms} contour maps for the $6M_1$ and 2H martensites are presented in Figure 1 c and d.

Although elastic anisotropy has been quantified in Cu-based SMAs [26,31,32], the composition used in this work is relatively less studied and no tabulated elastic constants were found in the literature. Instead we use the elastic constants of the closely related $Cu_{67.5}Al_{25}Mn_{7.5}$ alloy presented by Prasetyo et al. [33]. The elastic anisotropy parameter for this material in the DO_3 phase is $A = 2C_{44}/(C_{11}-C_{12}) = 10.9$ where C_{11}= 135, C_{12}=118, C_{44}=92.5 GPa.

3. Alloy and experimental methodology

A master alloy with composition Cu-23.2Al-3Ni-4.6Mn (at. %) was produced by melting high purity (99.9 wt.%) elemental powders under an Argon atmosphere in a sealed quartz tube. Wires with circular cross-sections of ~200 μm diameter and a few meters long were obtained by melt-ejection onto a rotating drum filled with water at 325 rpm, from a melt temperature of ~1300 °C, using a rotating drum wire caster (PSI Ltd. England) described elsewhere [34]. To promote β phase formation, the as-produced wires were annealed at 800 °C for 3 h under an argon atmosphere and water quenched. Differential scanning calorimetry (DSC) at 10 K/min was used to identify the transformation temperatures (Fig. 2), A_f ≈ -20 °C, A_s ≈ -41 °C, M_s ≈ -36 °C and M_f ≈ −55 °C (austenite finish and start and martensite start and finish, respectively). As evidenced by the DSC measurements, the alloy is austenitic at room temperature, and as a consequence superelastic behavior may be expected during compression. Further evidence of the single phase microstructure was obtained by X-ray diffraction (not shown), where all the peaks observed belonged to the austenitic β-phase.

The wires were cut to about 3 cm in length, embedded in a conductive resin, and ground and polished through a series of finer grit sizes to a mirror-like appearance using 0.05 μm colloidal silica for the final step. Grain orientations were determined by electron backscatter diffraction (EBSD) on a FEI XL-30 scanning electron microscope (SEM). Figure 3a is an SEM image of a wire with a diameter that ranges from 180 to 200 μm. The corresponding EBSD data is presented in Figure 3b. Grains with different orientations ranging from 100 to 400 μm in size can be observed, and from each grain various micropillars could be milled. Micromachining of cylindrical microcompression samples was conducted using a Helios Nanolab 600 Dual Beam Focused Ion Beam (FIB) Milling System at 30 kV accelerating voltage with currents ranging from 9.3 to 28 pA. A 40 μm diameter trench was milled around the pillar to a depth of ~2 μm, to provide clearance for micromechanical testing. Cylindrical pillars were produced with diameters varying from 1.4 to 2.2 μm, a range over which we observed no significant size effect. For instance, for a single orientation, comparing pillars of diameter 1.6 and 2.1 μm, we measured a transformation stress of 151 and 153 MPa, respectively, and a strain of 3.96 and 3.64%, respectively; we conclude that over the narrow range of sample sizes tested here, size effects between our data points can be neglected to first order. The aspect ratios were kept between 2 and 3. Within this range, the influence of pillar aspect ratios was found to be negligible in agreement with Refs. [35,36].

Micro-compression tests were carried out at 18°C (~ 38 °C above A_f) on a Hysitron Triboindenter using a 20 μm diameter cono-spherical tip under open-loop load control at 250 μN/s loading rate up to the maximum programmed load, followed by unloading at the same rate. This process was repeated multiple

times on a given pillar, increasing the maximum programmed load (P_{max}) on each cycle until failure occurred. After every second cycle, the tip positioning was checked by scanning the surface in contact profilometer mode, to address any possible sample drift; the tip was recentered on the pillar when necessary. For comparison purposes, load-displacement data was converted to stress-strain data using the mean diameter and the change in height of the pillar. To minimize errors in the stress-strain calculations arising from pillar taper, the diameter at the half of the pillar height was used instead of the diameter at the top of the pillar, but it should be borne in mind that the true stress state in these pillars is not perfectly uniform and this is a source of uncertainty in the discussion.

A typical superelastic response curve for a single pillar is shown in Fig. 4a. In order to experimentally determine the maximum transformation strain (ε_{max}) and the stress required to induce the martensite transformation (σ_{Ms}) for each pillar, we systematically probed at increasing stress levels. The maximum transformation strain was determined by examining the series and identifying the applied load level at which there was significant permanent deformation after unloading. Fig. 4b shows such a series of data from a typical pillar, where the increasing-load series leads to increasing total strains with essentially no residual strains after unloading up to a certain load level (i.e., superelasticity). When the total strain reaches around 6%, the degree of permanent deformation sharply increases, indicating that the applied load has exhausted the recoverable transformation strain, and begun to yield the pillar. The cycle exhibiting the highest total strain with the minimum permanent strain was selected (for example the test shown by an arrow in Fig. 4b) to assign the maximum transformation strain. For the same cycle, the critical stress for martensite transformation was recorded as shown in Fig. 4a, assessed as shown by a tangent construction on the linear elastic and transformation plateau portions of the curve. A similar construction was used to assess all of the critical stresses, as also shown for martensite finish, austenite start and finish. In what follows, we limit our discussion to these curves, i.e., those that just exhaust the full available transformation strain without inducing much plasticity, unless otherwise noted.

For comparison purposes, the bulk superleastic response of another segment of the as-cast polycrystalline wire with a cross sectional diameter of ~180 μm and 7.8 mm length was measured using a dynamical mechanical analyzer (DMA, TA Instruments Q800). DMA measurement was conducted by applying uniaxial tensile force with $3x10^{-4}$ s^{-1} strain rate at 20 °C.

4. Experimental Results

Figure 5a shows all the pillars experimentally tested in this work in a stereographic triangle showing the pillar axis orientation before loading (in austenite). The orientations are labeled with a “p” followed by the angle (in degrees) between [001] and the pillar axis. The pillars are also color-coded, with [111] [101] and [001] setting the color scales for blue, green, and red, respectively. Representative stress-strain curves of some selected grain orientations are presented in Figure 5b. Dissimilar mechanical responses are immediately observed depending on the orientation: different slopes of the initial linear elastic part of the loading curve, different transformation strains and different stresses required to induce the transformation. Larger transformation strains and lower transformation stresses are achieved in the pillars oriented near the [001] pole, while those closer to [111] exhibit smaller transformation strains at much larger transformation stresses. For instance, the critical stress to induce the martensitic

transformation, σ_{Ms}, for a near-[001] oriented pillar is only σ_{Ms} ~130 MPa, and total recoverable strains larger than 7 % are observed. Conversely, for a near-[101] orientation, σ_{Ms} is almost 400 MPa and the total strain is only ~2.5 %.

In order to highlight some of the differences in the properties of the principal orientations, pillars oriented close to [111], [101] and [001] directions are examined further in Fig. 6, where a sequence of increasing load cycles is presented. Comparison of the three orientations reveals differences in terms of shapes of the curves, permanent deformation, as well as transformation stresses and strains. The pillar milled closest to the [111] direction (Fig. 6a) exhibits almost no evidence of superelasticity and plastic deformation dominates the compressive response on every cycle. Different behavior is observed in the [101] oriented pillar, where hardening is detected during the martensite transformation, larger recoverable strains are achieved, but permanent strains eventually appear as the applied load increases. In the [001] oriented pillar (Fig. 6c) a single plateau is observed for low applied loads, transitioning to a series of plateaus in a staircase-like trace as the load is increased. The series of transformation bursts is likely due to a sequence of domains of transformation operating independently and in increasing order of energetic preference [18]. For this pillar, the strains are fully recovered to large values and no significant plasticity is observed in Fig. 6c.

In addition to the difference observed between the samples in Figs. 6a-c, there are also some signatures of an evolving response with cycle number. There is, for example, a tendency for both the slope of the loading curve and the critical transformation stress to decrease as the number of cycles rises; this is especially clear in Fig. 6c where the transformation is more pronounced. Such a decrease in the apparent loading modulus has been seen before, and related to the ease in martensite nucleation near the contact point with the indenter tip, which leads to a localized transformation that superimposes a small transformation strain upon the elastic response of the austenite [16]. On the other hand, the decrease of the critical transformation stress has been attributed by San Juan et al. [16,18] to a conventional shape memory "training" process, where the variant patterns that form are becoming more regular as the defect substructure evolves.

5. Comparison between calculated and experimental results

To correlate the theoretical calculations with the experimental results requires an assumption regarding which martensite phase is forming in the pillars. Prior authors have proposed that the phase that forms is the one with the largest ε_{tr}, and validated it using experiments in tension as well as in compression in a Cu-Al-Ni alloy [32]. Table 2 shows the theoretical ε_{tr} values for the cases of orthorhombic (2H) and monoclinic ($6M_1$) transformations, as well as the experimentally measured strains for the differently oriented pillars investigated in this study. Under the above assumption, in all the tested pillars except for p2.4 and p8.9, the $6M_1$ monoclinic phase is expected to have the larger strain, and thus is expected to be the one that will form under compressive loading. However, we note that there are a number of cases where both the $6M_1$ and 2H transformations result in similar values of ε_{tr}. In these cases, a mixture of both martensite structures could also be possible.

In Fig. 7a the experimental transformation strain is plotted against the calculated one for each orientation. It is interesting to note that although the trend in the data is as expected, the experimental values are considerably lower than the calculated ones. This is not the first time that lower strains have been observed in micropillars when compared to bulk expectations [10,12,13,19]. The discrepancy can most likely be attributed to geometrical effects: in a micropillar with a rigid constraint at the pillar base, the lower portion of the specimen is less likely to transform, and this could easily account for a systematic suppression of ~2-3% transformation strain. Clear evidence of partial transformation was recently reported by Zeng et al. [37] by imaging the pillar surface morphology after the transformation. The authors observed incomplete transformation due to constraints at the top, bottom and, in some cases, also in the pillar midsection. Taking into account the transformed fraction, they were able to correct the axial transformation strain and a reasonable agreement between theory and experiments was encountered. Alternatively, the starvation of martensite nucleation sites in small samples (i.e. grain boundaries, stress-concentrating surface defects, dislocations, etc.) has also been proposed by some authors, and could be related to some untransformed pillar regions where no nucleation points exist [13,38]. However, we note that San Juan et al. [39] achieved much larger transformation strains nearly matching the expected value of 8.6% in (001) Cu-Al-Ni oriented pillars of a larger diameter using the same micromechanical test instrument. These authors [39] used a rather sharp sphero-conical diamond indenter tip of 1.2 μm diameter, which caused plastic deformation, i.e. a large number of dislocations at the top surface when the pillar is relatively large (~2μm diameter) [17] as a result of the complex stress fields under the tip, which acted as martensite nucleation sites for the subsequent superelastic cycles; as a result, the critical stress and the transformation strain observed were about the same as in bulk-single crystals and no size effect was observed. Conversely, similar plastic deformation at the top of the pillar was not observed when the same authors tested sub-micrometer pillars. In that condition, the larger size of the indenter tip compared to the pillar diameter (~ 900 nm) and the lower forces required to induce the transformation combined to lower the stress concentration at the tip contact point. This limits plastic deformation, limiting the local dislocation content and resulting in the absence of nucleation points; larger stresses are thus required to induce the transformation. Similarly, in the present work a much blunter 20 μm diameter sphero-conical tip was used, which should nominally limit plastic deformation at the top of the pillar, and result in larger transformation stresses which, in turn, will result in lower transformation strains as commonly observed at the micro-/nanoscale [10,12,13].

In Fig. 7b the experimental and calculated transformation stresses are compared. Although the general trend of the data points aligns with the expectation of theory, the experimental transformation stresses are all larger than the calculated ones. This is likely due to the well documented size effect wherein the transformation stress rises in smaller pillars, and the theoretical σ_{Ms} values in our analysis do not account for any size effects on martensite formation. Pillars p39.7 and p38.9 (both oriented close to the (101) pole) and p46.6 (oriented close to the (111) pole) show a remarkably inflated critical stress, almost double the theoretical one. However, the transformation in these cases seems to be partially precluded by hardening and yielding accompanying the transformation (cf. Fig 6b).

The size effect arguments above become more evident when the stress-strain response of the 180 μm diameter polycrystalline wire is compared to that of the pillars milled from another segment of the same

wire. The stereographic triangle in the inset of Fig. 8a shows the orientation of the grains, which is quite random. Accordingly, we can estimate the expected, theoretical transformation stress using the Claussius-Clapeyron equation for randomly oriented crystals, with an average transformation strain of 6.66 % as calculated by Šittner and V. Novák; the result is an expected martensite start stress of ~115 MPa [40]. As shown in Figure 8a, a martensite start stress (σ_{Ms}) of 97 MPa was measured from this wire, which presents reasonably good agreement with the calculated value.

For the pillars machined from the same wire, even the most favorable orientation, i.e. the one that transforms under the lowest stress (125 MPa) is stronger than the bulk sample (~100 MPa). This is true in spite of the fact that the larger wire is also polycrystalline, and might thus be expected to have an increased transformation stress due to grain boundary constraints. We believe that this result is a reflection of a sample size effect: the pillars have a higher transformation stress than the wire from which they are made even after accounting for orientation effects and the effects of grain boundaries. In a broad sense, our observations are like those seen in other microcompression studies on SMAs. In other words, larger stresses are required to induce the martensitic transformation in micropillars than in their bulk counterparts. For example, in Ni-Fe-Ga pillars, the compressive stress necessary to induce the martensitic transformation was found to double when the pillar size is an order of magnitude smaller (e.g. 10 μm vs 1 μm) [13]. Similar trends were observed by San Juan et al., where the critical stress for a [001] single crystal of Cu-Al-Ni was 17 MPa, the critical stress almost an order of magnitude higher, σ_{Ms} = 147 MPa, for a 900 nm mean diameter pillar [17]. Irreversible strains after unloading have also been seen in prior studies on micropillar SMAs when the loading conditions lead to plasticity [12,13].

A requirement to obtain a reversible martensitic transformation, besides merely a low transformation stress, is also a high slip resistance in the parent austenite, to avoid deformation during (or instead of) the transformation. In our experiments, larger irreversible strains were observed at the beginning of the transformation for the (111) and (101) oriented pillars (Fig. 6 a-b). At the macroscale, such irreversible strains are commonly attributed to plastic deformation of martensite as a result of the large σ_{Ms} which may exceed the yield stress of the product phase and therefore trigger dislocation activity within it even as it is formed. This is certainly a plausible explanation for the behavior seen in our experiments in Fig. 6a and b. However, there is no reason to rule out plasticity in the austenite phase as contributing to this response, especially since in some of our experiments it seems that there may be unrecovered strains even when it is not clear that the transformation has occurred at all (cf. Fig. 6a). In fact, TEM studies support the notion that austenite plasticity may occur at similar stress levels to the transformation [12,41].

As a final point, a comparison between experimental and calculated Young's moduli of austenite, based on the initial loading curve, is presented in Figure 9. The general trend of the experiments aligns well with expectations, but the magnitude of the experimental modulus is considerably lower than nominally expected for most orientations, with greater disagreement as the orientation deviates further from [001]. In fact, there is reasonable agreement between the observed Young's modulus (E_{meas} = 20.5 GPa) and the calculated one (E_{calc} = 23.5 GPa) for pillars oriented close to the [001] pole. Away from [001] the difference becomes larger than the measurement itself, e.g., E_{calc} is 138.5 GPa while the E_{meas} is about 50 GPa for p46.6. We believe that this discrepancy is similar to the well-known increase of compliance in micropillars, which is largely due to punching of the pillar into the substrate, and which can be corrected for using

Sneddon's analysis [36, 42]. Such discrepancies are usually enhanced in the stiffer orientations of anisotropic materials. Plastic sink-in around our pillars is evidenced in Figure 10, where pillar imaging before (Fig. 10 a and c) and after compression (Fig. 10 b and d) in two different orientations is shown. Plastic deformation at the top of the pillar and also plastic sink-in can be detected in p46.6 after compression (Fig. 10a, b), which correlates as expected with a lower measured elastic modulus. On the other hand, the pillar oriented close to [001] (p2.4, Fig. 10c, d), preserves practically the same aspect ratio and does not show signs of plastic sink-in. Thus, the orientations that exhibit the largest modulus anomalies are those in which plastic sink-in is clearly observed.

6. Conclusions

A systematic study of orientation dependence in the superelastic response in a Cu-based shape memory alloy is presented based on micropillar compression tests. The main conclusions from this work are as follows:

- As in bulk Cu-Al-Ni single crystals, high elastic anisotropy and transformation anisotropy is observed in CuAlMnNi micropillars; dissimilar mechanical response is observed depending on the orientation.
- In micropillars oriented close to the (001) pole, good agreement between the experimental and calculated transformation stresses and Young's modulus can be observed; however, experimentally observed transformation strains are always lower than the calculated ones. We attribute this difference to the untransformed region in pillars that are constrained by the substrate.
- In orientations closer to (111) and (101) poles, in addition to the lower transformation strains, lower Young's modulus and considerably larger transformation stresses are observed when compared to the theoretically calculated ones. While the much lower Young's modulus observed in the stiffer orientations can be explained by plastic sink-in observed by SEM after compression around the pillars, the higher transformation stresses are attributed to a sample size effect. This result is supported by a test on a bulk specimen of the sample material from which the pillars were machined.

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BIBLIOGRAPHY

[1] U.S. Mallik, V. Sampath, Influence of aluminum and manganese concentration on the shape memory characteristics of Cu–Al–Mn shape memory alloys, J. Alloys and Comp. 459 (2008) 142-147.

[2] U.S. Mallik, V. Sampath, Influence of quaternary alloying additions on transformation temperatures and shape memory properties of Cu–Al–Mn shape memory alloy, J. Alloy Comp. 469 (2009) 156-163.

[3] K. Otsuka, K. Nakai, K. Shimizu, Structure dependence of superelasticity in Cu-Al-Ni Alloy, Scripta Metall. 8 (1974) 913-918.

[4] J.-L. Liu, H.-Y. Huang, J.-X. Xie, Superelastic anisotropy characteristics of columnar-grained Cu–Al–Mn shape memory alloys and its potential applications, Mater. Des. 85 (2015) 211–220.

[5] S. Miyazaki, K. Otsuka, Development of shape memory alloys, ISIJ Int. 29 (1989) 353-377.

[6] H. Horikawa, S. Ichinose, K. Morii, S. Miyazaki, K. Otsuka, Orientation dependence of β1→ β1′ stress-induced martensitic transformation in a Cu-AI-Ni alloy, Metall. Trans. 19A (1988) 915-923.

[7] L. Orégas, D. Favier, Stress-induced martensitic transformation of a NiTi alloy in isothermal shear, tensión and compression, Acta Mater. 46 (1998) 5579-5591.

[8] R.F. Hamilton, H. Sehitoglu, C. Efstathiou, H.J. Maier, Y. Chumlyakov, Pseudoelasticity in Co-Ni-Al single and polycrystals, Acta Mater. 54 (2006) 587-599.

[9] K. Gall, H. Sehitoglu, Y.I. Chumlyakov, I. Kireeva, Tension-compression asymmetry of the stress-strain response in aged single crystal and polycrystalline NiTi, Acta Mater. 47 (1999) 1203-1217.

[10] C.P. Frick, S. Orso, E. Arzt, Loss of pseudoelasticity in nickel–titanium sub-micron compression pillars, Acta Mater. 55 (2007) 3845-3855.

[11] J.M. San Juan, M.L. Nó, Superelasticity and shape memory at nano-scale: Size effects on the martensitic transformation, J. Alloy Compd. 577 (2013) S25-S29.

[12] J. Pfetzing-Micklich, R. Ghisleni, T. Simon, C. Somsen, J. Michler, G. Eggeler, Orientation dependence of stress-induced phase transformation and dislocation plasticity in NiTi shape memory alloys on the micro scale, Mat. Sci. Eng. A 538 (2012) 265-271.

[13] N. Ozdemir, I. Karaman, N.A. Mara, Y.I. Chumlyakov, H.E. Karaca, Size effects in the superelastic response of Ni54Fe19Ga27 shape memory alloy pillars with a two stage martensitic transformation, Acta Mater. 60 (2012) 5670-5685.

[14] D.M. Norfleet, P.M. Sarosi, S. Manchiraju, M.F.-X. Wagner, M.D. Uchic, P.M. Anderson, M.J. Mills, Transformation-induced plasticity during pseudoelastic deformation in Ni–Ti microcrystals, Acta Mater. 57 (2009) 3549-3561.

[15] J.M. San Juan, M.L. No, C.A. Schuh, Superelasticity and shape memory in micro- and nanometer-scale pillars, Adv. Mater. 20 (2008) 272-278.

[16] J.M. San Juan, J.F. Gómez-Cortés, G.A. López, C. Jiao, M.L. Nó, Long-term superelastic cycling at nano-scale in Cu-Al-Ni shape memory alloy micropillars, Appl. Phys. Lett. 104 (2014) 011901.

[17] J.M. San Juan, M.L. Nó, C.A. Schuh, Nanoscale shape-memory alloys for ultrahigh mechanical damping, Nat. Nanotechnol. 4 (2009) 415-419.

[18] J.M. San Juan, M. No, C.A. Schuh, Superelastic cycling of Cu-Al-Ni shape memory alloy micropillars, Acta Mater. 60 (2012) 4093-4106.

[19] C.P. Frick, B.G. Clark, S. Orso, P. Sonnweber-Ribic, E. Arzt, Orientation-independent pseudoelasticity in small-scale NiTi compression pillars, Scripta Mater. 59 (2008) 7-10.

[20] J.M. San Juan, M. No, C.A. Schuh, Thermomechanical behavior at the nanoscale and size effects in shape memory alloys, J. Mater. Res. 26 (2011) 2461-2469.

[21] M. Reinhold, D. Kiener, W. B. Knowlton, G. Dehm, P. Müllner, Deformation twinning in Ni–Mn–Ga micropillars with 10M martensite, Appl. Phys. Lett. 106 (2009) 053906.

[22] D.C. Dunand, P. Müllner, Size effects on magnetic actuation in Ni-Mn-Ga shape memory alloys, Adv Mater. 23 (2011) 216-232.

[23] N. Zárubová, V. Novák, Phase stability of CuAlMn shape memory alloys, Mat. Sci. Eng. A 378 (2004) 216-221.

[24] K. Otsuka, T. Ohba, M. Tokonami, C.M. Wayman, New description of long period stacking order structures of martensites in β-phase alloys, Scripta Metall. Mater. 29 (1993) 1359-1364.

[25] S. Stupkiewicz, Micromechanics of contact and interphase layers, Thesis dissertation, IPPT, PAN, Warszawa 2005.

[26] C.E. Sobrero, P. La Roca, A. Roatta, R.E. Bolmaro, J. Malarría, Shape memory properties of highly textured Cu–Al–Ni–(Ti) alloys, Mat. Sci. Eng. A 536 (2012) Pages 207-215.

[27] R.D. James, K.F. Hane, Martensitic transformations and shape memory materials, Acta Mater 48 (2000) 197-222.

[28] K Otsuka, M Tokonami, K Shimizu, Y Iwata, I Shibuya, Structure analysis of stress-induced β1 martensite in a Cu-Al-Ni alloy by neutron diffraction, Acta Metall. 27 (1979) 965-972.

[29] M.J Duggin, Further studies of martensitic transformations in gold-copper-zinc and copper-aluminium-nickel alloys, Acta Metall. 14 (1966) 123-129.

[30] J. Ortín, Ll. Mañosa, C.M. Friend, A. Planes, M. Yoshikawa, Calorimetric measurements on the β⇌γ' and β⇌β'martensitic transformations in a cu-al-ni single crystal subjected to uniaxial tensile stress, Philos. Mag. A 65 (1992) 461-475.

[31] V. Novák, P. Šittner, N. Zárubová, Anisotropy of transformation characteristics of Cu-base shape memory alloys, Mat. Sci. Eng. A 234–236 (1997) 414-417.

[32] V. Novák, P. Šittner, D. Vokoun, N. Zárubová, On the anisotropy of martensitic transformations in Cu-based alloys, Mat. Sci. Eng. A 273–275 (1999) 280-285.

[33] A. Prasetyo, F. Reynaud, H. Warlimont, Elastic constant anomalies and precipitation of an omega phase in some metastable Cu2 + xMn1−xAl B.C.C. alloys, Acta Metall. 24 (1976) 651-658.

[34] N. Tuncer, C.A. Schuh, Melt-cast microfibers of Cu-based shape memory alloy adopt a favorable texture for superelasticity, Scripta Mater. 117 (2016) 46–50.

[35] E.A. Peraza Hernandez, D.C. Lagoudas, Modeling size effects on the transformation behavior of shape memory alloy micropillars, J. Micromech. Microeng. 25 (2015) 075001.

[36] H. Zhang, B.E. Schuster, Q. Wei, K.T. Ramesh, The design of accurate micro-compression experiments, Scripta Mater. 54 (2006) 181-186.

[37] X.M. Zeng, A. Lai, C.L. Gan, C.A. Schuh, Crystal orientation dependence of the stress-induced martensitic transformation in zirconia-based shape memory ceramics, Acta Mater 116 (2016) 124-135.

[38] S. Ueland, Y. Chen, C.A. Schuh, Oligocrystalline Shape Memory Alloys, Adv. Funct. Mater. 22 (2012) 2094-2099.

[39] J. San Juan, M.L. Nó, Superelasticity and shape memory at nano-scale: Size effects on the martensitic transformation, J. Alloy Comp. 577S (2013) S25-S29.

[40] P. Šittner, V. Novák, Anisotropy of martensitic transformations in modeling of shape memory alloy polycrystals, Int. J. Plasticity 16 (2000) 1243-1268.

[41]T. Simon, A. Kröger, C. Somsen, A. Dlouhy, G. Eggeler, On the multiplication of dislocations during martensitic transformations in NiTi shape memory alloys, Acta Mater. 58 (2010) 1850-1860.

[42] I. N. Sneddon, The relation between load and penetration in the axisymmetric boussinesq problem for a punch of arbitrary profile, Int. J. Engng. Sci. 3 (1965) 47-57.

Figure Captions:

Fig. 1: Orientation distributions of transformation strain induced by (a) $\beta \rightarrow 6M_1$ and b) $\beta \rightarrow$ 2H transformations. These contour plots were translated into transformation stress (σ_{Ms}) contour plots for (c) $\beta \rightarrow 6M_1$ and (d) $\beta \rightarrow$ 2H transformations by using the Claussius-Clapeyron equation.

Fig.2: Heat absorption and release during heating and cooling, respectively, revealed by a DSC scan showing transformation temperatures.

Fig. 3: a) Scanning electron microscope (SEM) image of a Cu–Al–Mn-Ni wire. b) corresponding EBSD image (inset: inverse pole figure orientation legend, showing the crystal orientation with reference to the loading axis).

Fig. 4: a) Representative stress-strain curve for pillar p8.9. b) Evolution of permanent strain with total applied strain for the cycles performed on pillar p8.9. The shaded circle (marked with an arrow) shows that above a critical total applied strain, permanent strain starts to increase rapidly. This is the cycle selected to represent this orientation, which is taken as exhausting the full achievable transformation strain.

Fig. 5: a) Stereographic triangle indicating the orientations of pillar axes tested in this study. b) microcompression test results for some pillar orientations from Fig. 5a).

Fig. 6: Stress-strain measurements for microcompression tests on pillars oriented closer to the a) [111], b) [101] and c) [001] poles.

Fig. 7: a) The transformation strains and b) stresses that were measured experimentally are well below and above, respectively, than the theoretically calculated values.

Fig. 8: Stress-strain response of a 180 μm diameter polycrystalline wire in tension. The inset is the stereographic triangle showing the orientations of the grains in reference to the loading axis.

Fig. 9: The calculated Young´s modulus and the experimental one. The linear fit of the experimental data shown by a dashed line shows that the experimentally measured values deviate further from the perfect correlation (shown by the solid line) at higher values.

Fig. 10: SEM image of p46.6 a) before and b) after compression (taken from another perspective). SEM image of p2.4 c) before and d) after compression. Plastic deformationa at the top of the pillar and plastic sink-in are observed in p46.6 while p2.4 preserves practically the same aspect-ratio.

Table 1: Lattice parameters and monoclinic angles for different unit cells of the austenite and martensitic phases.

Table 2: Experimental ε_{tr}, calculated ε_{tr} for $6M_1$ and 2H martensites, Experimental σ_{Ms} and calculated σ_{Ms} for 6M1 and 2H martensites.